BAKERIAN LECTURE.—*On the Statistical and Thermodynamical Relations of Radiant Energy.*

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It was surmised by a prominent school of thought in ancient times, it became absorbed into the mechanical philosophy of Newton, and it was at length established by the experiments and reasonings of Dalton and his contemporaries, that matter is not divisible without limit, but is constituted of an aggregate of discrete entities, all alike for the same homogeneous substance, and naturally extremely minute compared with our powers of direct perception. The smallest portion of matter which we can manipulate (at any rate until very recently) consists of a vast assemblage of molecules, of independent self-existing systems which exert dynamical influences on each other. The direct knowledge of matter that mankind can acquire is a knowledge of the average behaviour and relations of the crowd of molecules. To a sentient intelligence with perceptions of space and time minute enough to examine the individual molecules, each of them would probably appear as a *cosmos* in itself, influencing and influenced by others,—not unlike stars in a firmament.

The observed laws of nature are thus laws of averages—are statistical relations. Yet they are for practical purposes exact. To illustrate this in a way that will presently be of use let us imagine a row of urns whose apertures are of different areas, and let us consider how N objects will be distributed at random among them, assuming that the chance of an object getting into an urn is proportional to the area of its aperture, and is otherwise indifferent as regards them all. If the number of objects is not very large in comparison with the number of urns, no direct law of numbers emerges in this random distribution : though by the doctrine of probabilities we may calculate definitely the relative numbers of times that the various distributions will occur in a vast total number of cases, and this will represent the chances of recurrence of these distributions. The most likely arrangements are those ranging close around the equable distribution, in which the contents of the urns are proportional to their apertures. Those far removed therefrom are much less likely. When the number N is very great, a relatively small deviation from the equable distribution has an almost negligible chance of occurring. Equable distribution then assumes the aspect of a rigid law ; nevertheless occasionally in an æon it will be widely departed from. The abstract laws governing the extent and distribution of the various kinds of

deviations from the mean distribution constitute an important part of the theory of statistics, first explored and developed by J. Bernoulli.*

Relative frequency of occurrence of the various collocations among all the possibilities, that are equally open subject to the restrictions essential to the constitution of the system, is the sole criterion of statistical law : and when the numbers concerned are vast, it assumes a precise and absolute form.

This procedure for determining the natural distribution of objects must be applicable to every subject that has to do with indefinitely numerous assemblages of similar molecules. It is more fundamental than the test of the ultimate state employed by Maxwell and his successors in the theory of gases, that the steady state is the one having the property that it is not disturbed (departed from) owing to the mutual collisions or encounters of the molecules. Indeed, we can regard this latter procedure as being itself the test for the state of maximum probability, viz., that a slight derangement does not alter its constitution. The application of the present method seems to have been first attempted in gas theory by O. E. Meyer, but was soon after more effectively realised by Boltzmann (1877); in his lectures on gas theory, however, only a few pages are devoted to this aspect of the subject.†

It may be, and has been, objected that this mode of procedure in molecular physics is ambiguous and unreliable ; that different ways of calculating the chances lead to entirely different results, and that there is no certainty as to which method is to be preferred. Such discrepancies can, however, arise only because the imposed conditions of physical necessity (dynamical laws) restricting the distribution that would otherwise be entirely fortuitous must have been chosen differently in the cases compared. But there can be only one set of conditions that are right: the correct and tolerably complete formulation of the physical problem may be difficult, only to be attempted in simple cases, but the method is sound and, in general, no other method seems to be open. In the very simplest physical aggregates of molecules that we can consider, such as a gas where they are practically independent of each other, the restricting conditions are, of course, far more complex than in the ideally simple illustration of urns and balls above. But if we have got hold of the main necessary conditions restricting fortuitous distribution, even though a whole series of minor ones are ignored, we shall be able to deduce approximately the actual statistical relations: although every new condition that is recognised and introduced into the

* *Cf., e.g.,* Lord Rayleigh, "On James Bernoulli's Theorem in Probabilities," 'Phil. Mag.,' 1899 ; 'Collected Papers,' vol. 4, p. 370.

† 'Vorlesungen über Gas-Theorie,' 1895, pp. 39–42, referring back to a longer and less definite discussion in the original paper.

analysis will alter to some extent the whole circumstances. There is no rigorous finality; and this, in fact, corresponds to nature, where we never know all about an actual system of bodies, but have to refine it down into an ideal simple system capable of more exact specification, and then compare the deduced results with the phenomena of the natural system of which it is a limited representation, but one that we can learn gradually to make more and more complete as knowledge advances.

The method of statistical probability thus corresponds closely to the features of the experimental exploration of nature. We never get to complete knowledge of anything, however simple; but we seize upon prominent groups of uniformities or correlations, more or less isolated, and thus capable of analysis more or less approximately by themselves, with subsequent introduction of corrections representing the influence of the other groups.

There would be little utility in following out these statistical methods if they were confined to systems of molecules that have already settled down into steady distribution—to systems forming homogeneous bodies in thermal equilibrium. The methods of dynamics of solid and fluid systems have been fully elaborated, and practically cover that field. It is as regards the residuum of uncorrelated movements of the molecules that the statistical method is essential—those which are put aside in ordinary dynamics, yet are available and powerful to modify mechanical forces in bulk when there is difference of temperature, owing to the combined effects of their striving towards mobile equilibrium of distribution, of which uniformity of tempera- ture is the test. The laws of transformation of residual (thermal) energy must find their justification in this connection. The fundamental thermodynamic principle that thermal energy tends towards the equilibrium distribution, never by any chance spontaneously in the opposite direction, is itself a direct result of the discrete statistical point of view, and cannot otherwise be justified. The degradation of mechanically available energy is the progress towards its equable molecular distribution, a progress which cannot be undone by any operations on matter which do not rearrange the molecules; and the measure of the amount of degradation must rest ultimately on statistical principles.

The most salient aspect, in Boltzmann's hands, of the method of pure statistics in the theory of molecular distribution in gases is the expression of this fact. In Clausius' treatment of the principle of degradation of the energy, this principle becomes the principle of continual increase of the entropy, that being the name given to a definite thermodynamic function of the state of the system, specified statistically in terms of ordinary

physical *data*. The proposition, that a molecular system always tends in spontaneous change towards states of greater entropy, runs parallel to the principle that it always tends towards molecular distributions of greater probability subject to the restraints and laws that are inevitable. The entropy (η) is thus in some way a measure of the probability of the molecular collocation. By testing this idea on the known gas theory, Boltzmann arrived at the conclusion that $\eta = k \log \Pi$, where Π is the probability of the molecular collocation, and k is a universal constant to be suitably chosen in terms of fundamental units. And the present train of ideas is here corroborated; for this logarithmic law is just as it ought to be, in order to satisfy the condition that the entropies of independent systems are additive, the conjoint chance Π being obtained by multiplication of the independent partial chances.

Moreover, by thus defining η for molecular distributions in terms of Π, the idea of entropy is extended to systems of which the differential element of mass is not itself in statistical equilibrium, that is to systems in which the idea of temperature at a point is inapplicable. Such systems, for example, may be made up of superposed systems of different temperatures, which interpenetrate yet keep their energies separate. Radiations of different wave-lengths in a perfectly reflecting enclosure form a case in point: their energies remain isolated, and become averaged independently, unless some absorbing molecular matter is present which opens a path for interchange. It is, in fact, in the theory of natural radiation, where it was first applied by Planck, that the statistical method has been effective as suggesting inferences beyond what formal thermodynamics, involving the existence of temperature, could supply.

What follows may be regarded as an expansion and generalisation of ideas implied in Planck's analysis for the case of natural radiation; it will involve, however, a modification of Boltzmann's application to gas theory, such as is apparently necessary to a direct general view of the molecular significance of temperature. This quality, temperature, which we know directly through a special sense, has, in fact, so universal a *rôle* in physical equilibrium that a definition of it in terms of complex analytical formulas, such as is obtained in gas theory, can hardly represent the fundamental aspect of the subject. And the thermodynamic scale of Lord Kelvin, though providing a universal criterion, does so rather by utilising a dynamical property than by elucidating the essence of the quality that is measured.

In the case of radiation, some of the main features inviting explanation may be set out in stronger light as follows. Consider a homogeneous solid body with an internal cavity, all being in thermal equilibrium. The question was

put early in the history of thermodynamics, whether the radiation from its walls, across this cavity, may not institute inequalities of temperature, in contradiction to Carnot's principle. The necessary negation was provided in a very elegant paper by Clausius, in which he explained how, on the Hamiltonian theory of rays, there is an exact balance of exchanges; that each element of surface must radiate to any other element just as much energy as it receives back from the radiation of the latter, provided their intrinsic brightnesses are equal. Let us now suppose that just beneath the radiating skin of the cavity there is an interface adiabatic to radiation and conduction, having two small apertures which can be imagined to be opened, say by sliding shutters, thus establishing communication with the mass of the solid body. When they are opened, transmission of energy among the molecules of the body, including heat-conduction, comes into play, conjointly with radiation across the cavity. Why is it that when the two elements of surface are of equal brightness as regards radiation, they are also adapted for an equilibrium of exchanges by the other route, across the mass of the body— because, if they were not, there could be no state of equilibrium? Again, to take another case: if we have three different bodies, A, B, C, in a row, so that B is in contact with each of the others, and in equilibrium of exchange of thermal energy with both of them, why is it that when B is removed, and the other two are moved up into contact, there is no disturbance of the equilibrium of thermal exchange? Facts such as these suggest a settling down of the wandering elements of energy into an equilibrium, in which each body, or each region, takes its share according to its capacity: and the task at present attempted is simply the expansion of this idea of distribution into quantitative form.

The general thesis of which a development is here attempted is thus the molecular statistics of distributions of energy; and the method that will be followed may be foreshadowed in a general way as follows. Our complex physical system is capable of containing energy in various forms, with paths of transformation open between them. We may apportion the system which is the seat of the energy into elementary receptacles of energy as regards each form assumed by it, which we may call *cells*: and we may establish a relation between the extents (in a generalised sense) of these cells by the condition that they shall be of equal opportunity, that the element of disturbance possessing the element of energy under consideration is as likely in its travels to occupy any one of them as any other. Our test of equality of opportunity is the Euclidean test of equality of extent, namely, so-called superposition; when an element of disturbance of one type is transformed so as to be of another type, and its course is traced during the transforma-

tion, the regions which it occupies in its progress are regions of equal opportunity for that type, or, say, cells of equal extent. The term " region " is here used in the sense of geometry of many dimensions, which is familiar in generalised gas theory. The energy itself, belonging to the same element of disturbance whose progress is traced, may be different in two states of it; for the transformation from the one to the other may involve the addition of energy, either abstracted from the surrounding region or entering by work applied from without. Thus we may make a mathematical formulation in which the energy is made up of differential elements, which are of different amounts, ϵ_1, ϵ_2, ... ϵ_r, for the r possible states of the energy, in which it is distributed among equivalent cells of numbers N_1, N_2, ... N_r; and the problem is to find n_1, n_2, ... n_r, which are the numbers of elements of energy that, in the ultimate state of statistical equilibrium, will reside in these groups of cells respectively, subject to conservation of its total amount E. The chance of the distribution just expressed, being made up of independent chances, is proportional to the number of ways Π in which this statistical distribution can be realised, which is of the form

$$\Pi = F(N_1, n_1) F(N_2, n_2,)...F(N_r, n_r);$$

and in the natural distribution this product must be a maximum subject to the restriction

$$\epsilon_1 n_1 + \epsilon_2 n_2 + ... + \epsilon_r n_r = E, \text{ constant.}$$

This gives

$$\delta \log \Pi = \frac{F'(N_1, n_1)}{F(N_1, n_1)} \delta n_1 + ...;$$

which, therefore, must vanish at the maximum, subject to the condition

$$0 = \epsilon_1 \delta n_1 + \epsilon_2 \delta n_2 + ...$$

This requires that

$$\frac{F'(N_s, n_s)}{F(N_s, n_s)} = \vartheta \epsilon_s$$

for all values of s, where ϑ is an undetermined quantity, the same for all the sets of *cells*. We have thus been led to a quantity ϑ which, in the state of equilibrium of exchanges of molecular energy, is the same throughout all parts of the structure of the system. It can be none other than temperature ; or rather, the scale and length of degrees being still undefined, it is some function of temperature as measured on any convenient scale. The value of $F(N, n)$, the number of modes of distribution of n-like objects in N-like compartments is, following Planck, $(N+n-1)!/(N-1)!n!$, which, when N and n are very large numbers, by application of Stirling's approximation $n! = n^n e^{-n} \sqrt{2\pi n}$, assumes the form

$$F(N, n) = (N+n)^{N+n}/N^N n^n,$$

so that $\log F(N, n) = (N+n) \log(N+n) - N \log N - n \log n,$

and therefore $\qquad \epsilon\vartheta = \dfrac{d}{dn}\log{(\mathrm{F}, n)} = \log\dfrac{\mathrm{N}+n}{n},$

and, finally, $\qquad\qquad\qquad ne = \dfrac{\mathrm{N}\epsilon}{e^{\epsilon\vartheta}-1}.$

This becomes Planck's formula for natural radiation, with ϑ representing temperature, when the values of N and ϵ are substituted in terms of λ, and when another factor, λ^{-1}, is adjoined to reduce the value to the same unit range of wave-length in all cases, as *infra*.

On this skeleton of a general theory of temperature various remarks are to be made. In the first place, there are many dynamical principles to be satisfied throughout the progress of the elements of disturbances, in addition to the conservation of energy; as witness the elaborate dynamical discussions in gas theory. For example, linear and angular momenta must be conserved during the migrations of the elements. It may be recognised, however, that all such principles will be required and will be used up in determining the equivalence of the various sets of cells, among which the wandering elements of disturbance are distributed at random. Of this, in fact, gas theory offers a convenient illustration; there the dynamical principles governing encounters are not ignored, but are fully used up in the determination of the relative extents of equivalent cells of different types ($\delta u\ \delta v\ \delta w$), so that no conditions are outstanding except the constancy of the total energy and the constancy of the total number of molecules. The energies, together with the paths followed by the elements of the disturbance, which latter are needed to determine the cells, make everything determinate, and therefore cover the whole dynamical field. It is only in a few of the simpler cases that this procedure for mapping out cells can yet be carried out, notably gas theory and the theory of natural radiation; but the point gained is that they here fit into a general scheme of distribution of the uncorrelated elements of energy instead of being isolated fragments of molecular theory. Our specification of cells must remain, however, an imperfect and merely approximate one, to be modified and improved by each fresh addition to our knowledge of the system; but this is as it should be, for the available energy of thermodynamics is itself provisional in the sense that new discoveries may and do reveal stores previously inaccessible for mechanical purposes.

Again, the foundation here assigned to the universal concept of temperature rests on the implied hypothesis that the distributions of the various types of energy in the various sets of similar cells are independent chances, so that the total probability is their product. If that were not so, each type of energy could not have a temperature of its own—equal to that of every

other type with which a path of interchange is open, when the system is in equilibrium. On the other hand, if this be so, without limitation, each range of wave-length in an adiabatically isolated region of radiation, such as the radiation in the range between λ and $\lambda + \delta\lambda$, acquires its own temperature when it has become fortuitously distributed by reflexions at the boundaries; while to equalise the temperatures of the different ranges of wave-length the presence of some absorbing matter is required to act as a means of exchange. We have here an illustration in which the *same* region is occupied by distributions of energy of different temperatures; even if this extension is demurred to, the principles will still apply to the contents of *adjacent* regions.

Again, the necessity for associating different amounts of energy with the same unitary element of disturbance, as it passes into regions of cells of different types, may be illustrated from the circumstance that reversible physical operations in bulk, such as the adiabatic compression of a mass of gas, cannot alter the statistics of distribution of the energy : thus indicating that the energy put into the system by compression is distributed among the said unitary elements of disturbance.

The principle of independent chances as regards the distributions of the various types of energy requires, as already mentioned, a re-statement, in altered form, of Boltzmann's statistical determination of entropy for gas theory. Under natural conditions, however, concerning the relation of the amount of the element of energy to the extent of a cell, the final results are not sensibly affected; thus the validity of the ordinary principles of gas theory will not come into question. As regards the general underlying idea, it seems reasonable that the distribution of things of different types (*e.g.*, molecular groups within various velocity ranges $\delta u\,\delta v\,\delta w$ in gas theory), so far as concerns their manner of mere mixture among one another in space, has not direct physical significance, which was what Boltzmann assumed. What matters is rather the opposite, the extent of the region of cells within which the elements of each type of disturbance have play to spread out, in view of their freedom to adjust their relative quantities by transformation into and from other types, subject only to the condition of constancy of the total energy.

The procedure of Planck for the elucidation of the statistical relations of natural radiation, which we have attempted to generalise, depends essentially, as Lorentz remarked, on the assumption of a discrete or atomic constitution of energy ; and the indivisible element of energy, as estimated from the constants of the formula for natural radiation, proves to be of considerable amount, even compared with the energy of a molecule of a gas.

A somewhat similar implication survives in the present development; but it now appears in the form that the ratio of the energy element to the extent of the standard unit cell is an absolute physical quantity determined similarly by the observations on natural radiation. A theory of the present type, as Mr. Jeans has recently remarked, has more likelihood of being true in the limit, if there be one, in which the element of energy becomes indefinitely small, after the manner of an ordinary differential; thus, here it would be the limiting differential ratio of energy element to extent of cell that is somehow predetermined, but now without any implication that energy is itself constituted on an atomic basis.

In short, what is formulated in the cells, into which the system is divided, is equality of opportunity, not for elements of energy, but for elements of disturbance, which pass into different types during their progress while retaining their identity, and in so doing receive or lose energy. This gain or loss we must assume to occur according to definite laws, independent of the path of transition of the disturbance between the configurations under comparison. In self-contained dynamical systems this is secured as a corollary from the Hamiltonian principle of variation of the Action, after the manner of Liouville's theorem of differential invariance. In its more general aspect it may perhaps be justified by a cyclical argument, after the manner of Carnot's principle in the classical thermodynamics.

The enquiry obviously presents itself: What is the relation of the order of ideas here sketched to the Maxwell-Boltzmann principle of equipartition of the energy, on the average, among the various degrees of freedom of each dynamical system, with which it in effect is in contradiction? The answer must be that in this order of ideas the different degrees of freedom of the system represent and are replaced by cells, or receptacles for differential elements of energy, which are of *equal opportunity* or *extent* as regards an element of disturbance which retains its identity, because they enter absolutely alike and without any mutual influence into the dynamical relations. Whether the amount of the element of energy is the same for them all can be determined by following the course of an element of disturbance from one into the other, and ascertaining whether the amount of its energy has to change. If there were no collisions and no æther, different types of energy would be entirely isolated—there would be no transition; and even collisions operate not by contact, but involve fundamentally the æther as an elastic buffer. If, then, we may take it that vibratory disturbance passes from one molecule to another, or from one free period to another, by interchange across the æther during mutual encounter, a consideration of the process of emission and subsequent absorption of radiation ought to reveal how

the energy has to change in the transition. When this transition is effected, through the agency of the work of the pressure of radiation as the mode of change in free æther from one free period to another, it fits consistently into the above general scheme; and the energy elements of the statistics are, in fact, different while the opportunities are equal in all the modes of vibratory molecular freedom.*

It remains to give some account of the physical bases of the argument as applied to the special case of radiant energy. A ray or filament of light, even sensibly homogeneous and therefore of infinitesimal range ($\delta\lambda$) of wave-length, is not a train of uniform waves; but it is the aggregate of a vast complex of trains of limited lengths, coming from the various molecules that take part in the radiation. The ray is thus a statistical aggregate; and the statistical relations of molecular equilibrium that are implied in the existence of a temperature in the radiating element of mass will be transmitted in some form into the constitution of the ray, and will thus limit its generality if it is to belong to natural radiation.† An early way of representing this constitution was to consider the ray as a system of separate impulses or elements following one another; and the problem took the form of determining the limitations imposed on their character and succession in natural light in consequence of the molecular equilibrium in each element of the source. This problem seems to have been first essayed by W. Michelson in 1887; it was soon after developed by Lord Rayleigh‡ in various papers. We propose, in this way, to divide the natural ray or filament of light into a set of elements, one of which may be, *e.g.*, a short train of simple undulations; each of these elements of disturbance travels so that its content, measured by $\delta S\, \delta\omega$ per unit length (l) where δS is cross section and $\delta\omega$ solid angle of divergence at it, remains unchanged, in a manner that however involves a rather close interpretation of the idea of differential invariance.§ We may take $\delta S\, \delta\omega \,.\, l$ to be the measure of the extent of an æther-cell for radiation of the given period. To compare the extents of cells for different periods we

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* The investigation by Lorentz, in which the natural radiation of metals is deduced (for an ideal metal) as due to the deflections of free electrons, moving with the velocities of gas-theory, by collision with the molecules, is one of the ways in which radiation may be connected up with translatory molecular motions.

† *Cf.* "On the Constitution of Natural Radiation," 'Phil. Mag.,' Nov., 1905 : also recent investigations in the 'Annalen der Physik' by Planck, Laue, and others.

‡ *Cf.* "On the Character of the Complete Radiation at a given Temperature," 'Phil. Mag.,' vol. 27, 1889 ; 'Scientific Papers,' vol. 3, p. 268.

§ *Cf.* "On the Statistical Dynamics of Gas Theory as illustrated by Meteor Swarms and Optical Rays," 'Brit. Assoc. Report,' 1900 ; or 'Nature,' Dec. 27, 1900. But the analogy does not extend to reflection from a moving mirror, $\delta S\, \delta\omega$ not retaining its value for the reflected swarm of particles.

must follow the transition of a filament of disturbance from one period to another, say a higher one. The change can be imagined to be effected gradually, by shortening l by compression exerted by perfect reflectors working against the pressure of the radiation. It appears that energy is added so that the amount of energy in the filament of disturbance is always inversely as the wave length λ; while the extent of the cell containing it varies directly as λ^3. We assume that these relations, obtained in this special manner, are universal, relying for the evidence thereof in the simpler cases on dynamical theory and on special verification, but generally on a principle analogous to that of Carnot, as above. Then a statistical procedure on the lines sketched above gives for the densities of energy in corresponding infinitesimal ranges of wave-length the expression $C\lambda^{-4}/(e^{c_2/\lambda\vartheta}-1)$. But the extents of corresponding ranges $(\delta\lambda)$ are proportional to the mean wave-lengths (λ): thus the density of energy per unit range involves an additional factor λ^{-1}, and the constitution of natural radiation is given by the expression $E_\lambda\delta\lambda$, where

$$E_\lambda = C_1\lambda^{-5}/(e^{c_2/\lambda\vartheta}-1),$$

which is Planck's well-known formula.

The demonstration of these relations between the extents of cells occupied by the same filament of disturbance when it is transferred to different wave-lengths, and its energies, and its ranges $(\delta\lambda)$, is obtained by following out the circumstances of the oblique reflexion of a filament from an advancing perfect reflector. The relations thus obtained then form a basis, leading by pure statistical procedure, without admixture of extraneous thermodynamics, to the Planck law for natural radiation. This law of course includes the Stefan-Boltzmann law for the total radiant energy, and the Wien displacement law pertaining to the form of the energy-curve at different temperatures, which marked the limit of the knowledge derivable from the classical thermodynamics.

It may be recalled that the original demonstration of Wien's law involved the compression of a slice of natural radiation by approach of its totally reflecting parallel bounding walls, and a rather complex statistical re-classification of its elementary parts as thus altered. By Carnot's principle these parts must constitute the natural radiation at some other temperature: which leads to Wien's inference. The demonstration is reduced to the simplest and most direct terms by arguing from the special case of a volume of natural radiation enclosed in a spherical boundary which is gradually and uniformly shrunk. Here the wave-length of *each* elementary filament is altered in proportion to the radius of the boundary, and its energy in the inverse ratio; thus the statistical averages are not disturbed, and no process

of estimating them afresh is now required.* If the general statements above made hold good, not only do these relations hold for the spherical enclosure, but also each filament of radiation contained in it must occupy similar positions with regard to the boundary, at the end and at the beginning. This is readily proved independently, and it constitutes a confirmation of the preceding statements; for r being the radius, δS varies as r^2, and l varies as r, while $\delta\omega$ is as before, so that the extent $\delta S\,\delta\omega\,.\,l$ varies as r^3, that is as λ^3, while the energy involved varies as λ^{-1}.

We have now to consider how far it is feasible to extend these statistics of radiation so as to include the material molecules and their types of free vibration in the spectrum. If the type of vibration for a free period is that of a simple Hertzian bipole, it has been shown by Planck† that in a field of natural radiation specified per unit volume by $E_\lambda\delta\lambda$ (or by $cE_\lambda n^{-2}\delta n$, where n is the frequency) the average vibratory energy of a molecule for a free period of wave-length λ is $8\pi\lambda^{-4}E_\lambda$. We may thus say that the capacity or extent of the single molecular period is equal to that of a volume $8\pi\lambda^{-4}$ as regards the radiation, per unit range, near that wave-length. But this volume of free radiation specified by E_λ is equivalent in extent, by the mode of transformation above, to a volume $8\pi\lambda_1^{-4}$ of radiation specified by $E_{\lambda 1}$, which is again equivalent in extent to the energy in a free molecular period corresponding to λ_1. Thus the capacities, or opportunities, or extents, whichever term we prefer, are the same for all free molecular periods; but the elements of energy, namely those of the same disturbance as transformed from one into the other, are inversely as the wave-length.

In fact, different free periods are of equal opportunity for another reason, that of gas theory, because their vibrations are entirely independent and superposable; so that there is nothing to determine whether an element of disturbance locates itself in one or other of them. But in the process, spontaneous or not, of getting from one to another receptacle or cell, the disturbance has to absorb energy from the surrounding elements of disturbance, or reject it to them, in such manner that the unitary energy-elements are different for the two cells. It is the disturbance, here the element of radiation, that is an entity, identifiable in its wanderings, but the energy belonging to it may change as it passes from one location to another, just as in gas theory it is the molecule that can be traced from one group $(\delta u\ \delta v\ \delta w)$ to another, but its energy changes in the transition.

For very long wave-lengths the analysis shows that the elements of energy

* *Cf.* "On the Relations of Radiation to Temperature," 'Brit. Assoc. Report,' 1900; or 'Nature,' Dec. 27, 1900.

† *Cf.* also H. Lamb, 'Trans. Camb. Phil. Soc.,' Stokes Jubilee Vol., vol. 18, 1899, p. 349.

may be taken as practically of the same amount in all types of cells, so that the energy is distributed among the cells in proportion to their extents or opportunities,—equipartition holds good. The reiterated opinion of Lord Rayleigh may here be recalled, that the weakness of the usual argument for equipartition of the energy seems to lie in the unsatisfactory treatment of the potential energy residing in very powerful (*i.e.* almost rigid) restraints, such, namely, as involve very short times of relaxation.

Probably the most remarkable incident in the long discussions to which this subject has given rise has been a brief indication by Lord Rayleigh of how he would expect the energy to be partitioned—one which would have satisfied him completely were it not that it led to frittering away into higher periods without any final equilibrium. In this brief note* he obtained the correct value for long waves, practically by isolating in thought a rectangular block of æther, and considering all its possible modes of free vibration as excited with equipartition of energy, postulating that the natural radiation is made up of them all taken together—that is, made up as regards distribution of energy but by no means as regards configuration.†

In what relation does this very remarkable and successful *aperçu* stand to the ideas here sketched ? Its exposition and development have been essayed recently in several very interesting papers by Mr. Jeans,‡ and have been continued in this direction in Prof. Lorentz's Address on the present subject delivered to the last Mathematical Congress at Rome. The great obstacle *à posteriori* is, as aforesaid, the frittering away of the energy into the unlimited number of very high free vibrational periods. On the other side, the remark made above seems worthy of emphasis, that in such an illustrative system the energy does not distribute itself at all: it remains as it was originally, unless avenues for transformation are admitted ; whereas if means are so provided for one of the partial disturbances to alter its wave-length, it will alter its energy too, at the expense of its neighbours.

The problem which we have here essayed to discuss is, on one of its sides, of long standing. For more than thirty years, ever since Boltzmann and

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* 'Phil. Mag.,' vol. 49, 1900, pp. 139, 140 ; 'Scientific Papers,' vol. 4, pp. 483—485, with note of date 1902 indicating the subsequent experimental confirmation of his result for long waves. Planck subsequently pointed out that not merely the form, but also the numerical coefficient, was experimentally correct, agreeing with his own later formula ; for the procedure requires that the energy of each vibrational mode must be put equal to that of each translational mode of a molecule in a gas. *Cf.* Planck, 'Vorlesungen über die Theorie der Wärmestrahlung,' 1906, § 154.

† It may be noted that uniform compression of this very specially co-ordinated system alters all the energies in the inverse ratio of the linear dimensions.

‡ *Cf.* 'Phil. Mag.,' June, July, 1909.

Maxwell generalised the principle of equipartition of molecular energy, the resulting paradox has been urgently in need of unravelment. Lord Kelvin resolved it by denying that the analysis put forward involved any real contact with the principle it sought to establish, and afterwards spent much time in destructive criticism of special cases.* Lord Rayleigh has played throughout the part of umpire, warding off unfounded objections to the principle, while at the same time keeping an open mind regarding its validity: indeed hardly anything has been urged on the side of equipartition of energy that is not to be found in his two papers of 1892 and 1900.†

The motive of this present discussion is the conviction expressed at the beginning, that the statistical method, in Boltzmann's form, must in some way hold the key of the position, no other mode of treatment sufficiently general being available. The writer has held to this belief, with only partial means of justification, ever since the appearance in 1902 of Planck's early paper extending that method to radiation. In the 'British Association Report,' 1902, p. 546, there is a brief abstract of a communication "On the Application of the Method of Entropy to Radiant Energy," in which it was essayed to replace Planck's statistics of bipolar vibrators by statistics of elements of radiant disturbance. "It was explained that various difficulties attending this procedure are evaded and the same result obtained, by discarding the vibrators, and considering the random distribution of the permanent elements of the radiation itself, among the differential elements of volume of the enclosure, somewhat on the analogy of the Newtonian corpuscular theory of optics (*cf.* 'Brit. Assoc. Report,' 1900)."

Since that time the present point of view has been presented and discussed at various times in University lectures.‡ The writer has recently been encouraged, from various quarters, to offer the type of argument here very briefly, and perhaps obscurely, outlined, to the consideration of a wider audience, including the experts in this complex subject, which is so fundamental in molecular physics.

* *Cf.* his 'Baltimore Lectures,' *passim.*

† "Remarks on Maxwell's Investigation regarding Boltzmann's Theorem," 'Phil. Mag.,' vol. 33, 1892 ; 'Scientific Papers,' vol. 3, pp. 554—557. "On the Law of Partition of Kinetic Energy," 'Phil. Mag.,' vol. 49, 1900 ; 'Scientific Papers,' vol. 4, pp. 433—451.

‡ Among others, at Columbia University, New York, in March, 1907.